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The effects of H_2SO_4 and $(NH_4)_2SO_4$ treatments on the chemistry of soil drainage water and pine seedlings in forest soil microcosms

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Abstract

An experiment comparing effects of sulphuric acid and reduced N deposition on soil water quality and on chemical and physical growth indicators for forest ecosystems is described. Six H_2SO_4 and $(NH_4)_2SO_4$ treatment loads, from 0 – 44 and 0 – 25 $kmol_c\ ha^{-1}\ yr^{-1}$, respectively, were applied to outdoor microcosms of *Pinus sylvestris* seedlings in 3 acid to intermediate upland soils (calc-silicate, quartzite and granite) for 2 years. Different soil types responded similarly to H_2SO_4 loads, resulting in decreased leachate pH, but differently to reduced N inputs. In microcosms of calc-silicate soil, nitrification of NH_4 resulted in lower pH and higher cation leaching than in acid treatments. By contrast, in quartzite and granite soils, $(NH_4)_2SO_4$ promoted direct cation leaching, although leachate pH increased. The results highlighted the importance of soil composition on the nature of the cations leached, the SO_4 adsorption capacities and microbial N transformations. Greater seedling growth on calc-silicate soils under both treatment types was related to sustained nutrient availability. Reductions in foliar P and Mg with higher N treatments were observed for seedlings in the calc-silicate soil. There were few treatment effects on quartzite and granite microcosm tree seedlings since P limitation precluded seedling growth responses to treatments. Hence, any benefits of N deposition to seedlings on quartzite and granite soils appeared limited by availability of co-nutrients, exacerbated by rapid depletion of soil exchangeable base cations.

Keywords: acidification, manipulation, nitrogen, ammonium, deposition, soil, drainage, pine, microcosms, forest

Introduction

Although acid deposition is a well-documented environmental problem, the balance of the pollutant species is changing. Between 1990 and 1998, European emissions of sulphur have decreased by 41% (NEGTAP, 2001), whilst oxidised and reduced N species have shown smaller decreases of 21% and 14% respectively. The UNECE Gothenburg protocol targets industrially derived NO_x emissions, but legislation to reduce NH_x emissions remains difficult because of the diffuse agricultural sources (Sommer and Hutchings, 1995). In many European countries, reduced N species dominate total N deposition (NEGTAP, 2001).

Acidic deposition across Europe has been linked to forest dieback (Nihlgård, 1985; Pearson and Stuart, 1993). Acid deposition impacts on growth of conifers are variable and species-dependent (e.g. Percy, 1986); being generally related to conditions of low solution pH, leaching losses of base cations (Joslin *et al*., 1992), the mobilisation of Al and inhibited root and mycorrhizal growth and nutrient uptake (Rengel, 1992). Direct acidification of soils can be attributed to H^+ and SO_2 deposition. Correspondingly, N deposition may promote nutrient imbalances and generate protons through reduced N oxidation. In N-limited ecosystems, N deposition may initially stimulate growth and trigger unsustainable demand for other nutrients resulting in less biomass production (Nihlgård, 1985), ecosystem N saturation (e.g. Aber *et al*., 1989) and changes in plant species composition (Heil and Diemont, 1983; Van der Eerden *et al*., 1991). Nitrification has been documented as an important proton source (Van Breemen *et al*., 1982), which depends on soil and microbial factors (Vonk, 1987; Rudebeck and Persson, 1998). The resulting NO_3^- may

accelerate leaching of cations (Van Miegroet and Cole, 1984; Baba and Okazaki, 1998). Not all reduced N inputs are nitrified under unfavourable soil or microbial conditions, when NH_4^+ deposition is excessive (Vonk, 1987), or when other nutrients are limiting (Gundersen and Rasmussen, 1988). Retention of NH_4^+ on exchange sites facilitates losses of other cations (Skeffington and Wilson, 1988), whilst direct leaching of NH_4^+ into the plant root environment may trigger competition between uptake of NH_4^+ and other nutrient cations (Nilsson and Grennfelt, 1988).

The critical loads approach is now widely used to formulate international policy for control of sulphur and nitrogen emissions and their impacts on ecosystems. Initially, critical loads for S considered only acidification effects. However, current methods for N species are based largely on nutrient effects utilising either empirical or N saturation models (Nilsson and Grennfelt, 1988). To quantify critical loads for a target ecosystem (Posch and de Vries, 1999) a biological indicator is selected, along with a chemical criterion on which a critical threshold for damage may be set. However, debate continues, especially for nitrogen, about the most appropriate bio indicators and chemical criteria (Skeffington and Wilson, 1988; Posch and de Vries, 1999; NEGTAP, 2001).

An understanding of the interaction of atmospheric acidifying pollutant species with the soil plant ecosystem is especially important to forest sustainability in the UK, where much commercial forestry is located on acidification sensitive upland soils with little alternative agricultural potential.

This paper addresses the response of soil pine-seedling microcosms to two-years of treatment with different levels of deposition of sulphuric acid and ammonium sulphate in an open plot, the aims being to:

(i) assess the differences in the acidification response of three upland soils to these pollutant species at different loads;
(ii) assess the effects of seasonality in ambient climate and deposition on treatment interactions with the microcosms;
(iii) examine the sustainability of nutrient availability and chemical conditions for seedling growth and relate this to critical loads for these pollutants.

Seedlings were of Scots pine (*Pinus sylvestris*), a native species and one of the two most common plantation trees in the UK (Forestry Commission, 2001). The three soils were representative of low nutrient status soils common to moorland and upland locations where such species are predominantly planted. The present experimental procedure benefits over previous manipulation approaches by encompassing a realistic treatment/watering regime, variations in ambient climate and deposition, a low to high range of pollutant additions and high levels of replication.

Methods

SOIL COLLECTION AND CHARACTERISATION

The uppermost mineral soil material (A horizon) was collected at three freely drained moorland sites in north-east Scotland (Table 1) and each sieved to 1 cm, while field moist, to remove larger stones and roots and homogenise the material. Initial soil chemical characteristics were determined on sub-samples of homogenised soil. Soil pH was measured as 1:2.5 pastes in water and 0.01M $CaCl_2$. Organic matter content was calculated from loss on ignition (Ball, 1964). Exchangeable base cation concentrations were determined on triplicate samples using neutral ammonium acetate extraction, with cation exchange capacity sequentially determined by replacement of the bound NH_4^+ by leaching with acidified 1M NaCl. The C:N ratio was measured in triplicate on finely milled, dried samples (Fison CNS analyser).

Table 1. Characteristics of soil collection sites

Soil parent material	*OS grid ref*	*Geological unit* †	*Vegetation*	*Soil type*
Calc-silicate	NO 135831	Dolomitic limestone interbedded with psammite and pelite (sL^d_B)	*Nardus* sp., *Carex* sp., *Calluna vulgaris*	Cambisol
Quartzite	NO 159896	Feldspathic quartzite (Q^q_B)	*Calluna vulgaris*, *Sphagnum* sp.	Humus iron podzol
Granite	NO 614836	Granite (G_{GM6})	*Calluna vulgaris, Erica cinerea*	Humus iron podzol

†BGS (1995)

PLOT DESIGN

Soil-seedling microcosms, at approximate field bulk densities, were assembled in inert black HDPE plant pots (0.25 m depth, 0.26 m diameter), with large drainage holes. Two-year-old bare-rooted seedlings of *Pinus sylvestris* (Forestry Commission, Scotland, identity 96-2039, Region of provenance 20) were planted to a depth of 0.2 m, the roots having first been washed with water. Five replicates of the controls and each of the five levels of acid and ammonium treatments were used. The resulting 165 pots were laid out in a randomised block design, outdoors at the University of Aberdeen (coastal NE Scotland, 20 m a.s.l.). A plastic spacer collar elevated the microcosm pot above a lower pot, sunk into a gravel base, facilitating collection of drainage waters in plastic bags. The plot was left uncovered to achieve realistic environmental conditions.

TREATMENT LOADS AND APPLICATION

Treatments commenced in May 1999, with the microcosms having experienced ambient deposition only for the preceding month since being planting in April 1999. Total deposition comprised a combination of applied treatments and natural ambient deposition, applied as 635 ml weekly per pot onto the seedling and soil surface. Treatments comprised five incremental loadings of H_2SO_4 or $(NH_4)SO_4$ (Table 2a; treatments A1–A5 and N1–N5 respectively) superimposed upon an artificial Aberdeen rain chemical composition (reflected by the control composition) calculated from National Deposition Monitoring Network data supplied by CEH (Edinburgh), each microcosm receiving 1500 mm yr^{-1}. Control treatments (A0 or N0) received ambient deposition loads in addition to artificial deposition without added S or N species (Table 2). For comparison, wet deposited UK deposition ranges for 1997 (NEGTAP, 2001) were <0.2 – >0.6 $kmol_c$ (reduced N) ha^{-1} yr^{-1}, <0.2 – >0.8 $kmol_c$ (H) ha^{-1} yr^{-1} and <0.3 – 1.6 $kmol_c$ (S) ha^{-1} yr^{-1}. Mean annual ambient deposition loads (1995–97) at the soil collection sites are given in Table 2c (taken from Stutter *et al*., 2003).

Total ambient deposition for each sampling period (Fig. 1; bulk deposition concentrations multiplied by volume at the site) reflects considerable seasonality, strongly driven by changes in precipitation volume. Table 2 shows that depositional base cation sources were principally through ambient, rather than treatment inputs and that the total

Table 2. (a) treatment deposition loads to microcosms and treatment solution pH, (b) experimental site ambient deposition, and (c) soil collection site natural ambient deposition (loads expressed in units of $kmol_c$ ha^{-1} yr^{-1} and rainfall as mm yr^{-1}).

		Na	*K*	*Ca*	*Mg*	*NH_4*	*H*	*Cl*	*SO_4*	*NO_3*	*pH*	*Rainfall*
(A) TREATMENT DEPOSITION LOADS AND PH												650
Sulphuric	A1	1.5	0	0.2	0.4	0	1.4	2.0	1.4	0	3.7	
acid	A2	1.5	0	0.2	0.4	0	4.4	2.0	4.4	0	3.2	
	A3	1.5	0	0.2	0.4	0	7.3	2.0	7.3	0	2.9	
	A4	1.5	0	0.2	0.4	0	14	2.0	14	0	2.7	
	A5	1.5	0	0.2	0.4	0	44	2.0	44	0	2.2	
Ammonium	N1	1.5	0	0.2	0.4	1.5	0	2.0	1.5	0	nd	
sulphate	N2	1.5	0	0.2	0.4	2.8	0	2.0	2.8	0	nd	
	N3	1.5	0	0.2	0.4	5.9	0	2.0	5.9	0	nd	
	N4	1.5	0	0.2	0.4	12	0	2.0	12	0	nd	
	N5	1.5	0	0.2	0.4	25	0	2.0	25	0	nd	
Control	A0 / N0	1.5	0	0.2	0.4	0	0	1.8	0.2	0	5.2	
(B) AMBIENT DEPOSITION		2.2	0.2	1.2	0.7	0.3	0.04	2.4	0.7	0.7	nd	840
(C) SOIL COLLECTION SITE DEPOSITION (WET+DRY+OCCULT)												
Calc-silicate site		1.1	nd	0.2	0.4	0.4	0.5	1.7	0.8	0.4	nd	1140
Quartzite site	1.0	nd	0.2	0.4	0.4	0.4	1.5	0.8	0.4	nd	1005	
Granite site	1.4	nd	0.2	0.5	0.6	0.7	2.1	1.0	0.6	nd	1200	

'nd' denotes no data available

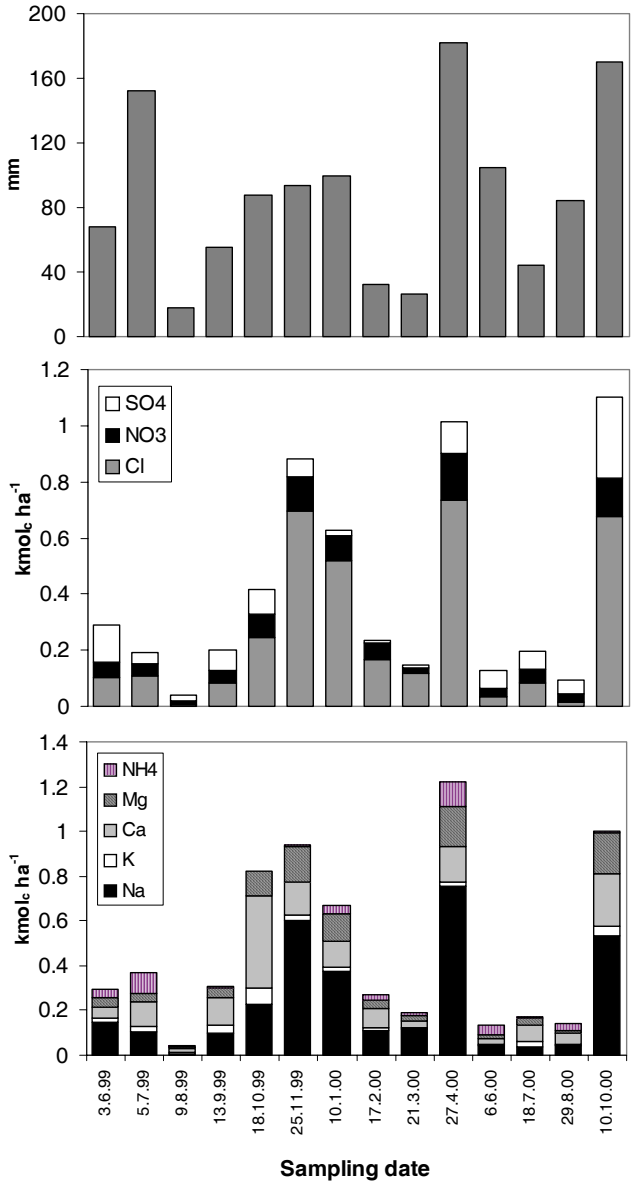

Fig. 1. (a) Ambient precipitation, (b) cation and (c) anion ambient deposition loads over each sampling period at the open experimental site in Aberdeen.

experimental base cation deposition exceeded that of the field sites, especially for Ca.

SAMPLING AND ANALYSIS

Drainage water chemistry

The experiment spanned two growing seasons (May 1999 – October 2000), during which 14 sets of regular samples were taken. Drainage waters were sampled 48 hours after application of that week's treatment. Total volumes were measured to enable flux calculations and sub-samples retained for analysis. A rain gauge, on site, was also sampled, and the total volume recorded.

Solution pH was determined within 24 hours and other analyses within a week of collection. Calcium and Mg were measured by atomic absorption spectroscopy (AAS), and Na and K by flame photometry. Total Al was measured by flame AAS (nitrous oxide-acetylene flame, with ionisation buffer) above 2 mg l^{-1}, or by furnace AAS (Perkin Elmer 3300 AAS with HGA 600 furnace) below 2 mg l^{-1}. Ammonium was determined by flow injection automated colorimetry and Cl^-, F^-, SO_4^{2-}, NO_3^- and PO_4^{3-} by Dionex ion chromatography on samples filtered to 0.45 µm.

Seedling biological measurements

Total height (stem base to tip of leading shoot) and stem base diameter (1 cm above ground using a digital calliper) were measured at the beginning of the experiment and after the first and second growth seasons (September 1999 and 2000).

At the end of the second growing season, 15–20 current year needles were harvested from each seedling, washed in deionised water, blotted dry and divided equally for chemical and chlorophyll analyses. Those for chlorophyll analyses, were finely cut and 1 g of tissue was homogenised twice in 82% ammoniacal acetone (81.8% acetone, 0.2% NH_4OH, 18% water) in a darkened room. The extracts were centrifuged at 1400 rpm for three minutes and stored prior to analysis in the dark at 4°C. The samples were diluted and absorbencies were measured at 645 nm and 663 nm by spectrophotometry (Hitachi U-2001). Chlorophyll a and b concentrations were calculated from these absorbencies (Hendry and Grime, 1993) and expressed in terms of fresh mass. Needles for chemical analyses of base cations and nutrients were analysed by the method of Cresser and Parsons (1979) and expressed on an oven dried weight basis.

Statistical analyses

Data were analysed using the statistics package Minitab 13.1, principally through ANOVA testing of soil and treatment level means (n = 5). Differences between control and treatment levels for chemical variables were further explored through Tukey simultaneous testing ($p \leq 0.05$). For simplicity, graphical presentations depict means (n = 5), with error bars omitted. Treatment types were generally analysed separately for simplicity. Statistical analyses of differences between the three soil types and the six treatment levels were felt to be of greater importance to the experimental aims. Hence, these comparisons are made within each individual treatment class and the contrasting inferences of these statistical results between treatment types are commented upon in the discussion.

Results

INITIAL SOIL CHEMICAL CHARACTERISTICS

Initial differences between soil types are shown in Table 3a. Soil pH values were low for the quartzite and granite soils. The calc-silicate soil had higher pH, but lower exchangeable base cation concentrations than the quartzite soil, however with a higher Ca % saturation. The quartzite and granite soils had higher organic matter contents and higher C:N ratios than the calc-silicate soil. The quartzite and granite soils had higher CEC values, probably attributed to organic exchange sites. The granite soil had the lowest base saturation and exchangeable cation concentrations, with the exception of Na.

The calc-silicate and quartzite soils were composed of coarser material than the granite soil, which had more silt-sized material (Table 3b). The mineralogy of the soils was similarly dominated by quartz. The calc-silicate soil originated from a mixed schist drift parent material. The term calc-silicate is used to describe it throughout since it contained more reactive minerals, including potential Ca and Mg sources from hornblende, biotite and secondary minerals in the trioctahedral clay group. The granite soil was the most acid and the quartzite soil intermediate, with greater contribution of dioctahedral alteration products such as illite, vermiculite or kaolinite.

SOIL LEACHATE CHEMISTRY

Time-series plots of leachate chemistry (Figs. 2-6) allow a comparative assessment of seasonal variation in chemistry resulting from the treatments. Separate ANOVA analyses within treatment type classes of leachate Ca and Mg concentrations and pH demonstrated soil type and treatment load as significant factors ($p \leq 0.001$) over every sampling date for both treatment types. For both treatment types, load became less significant for Na and K concentrations ($p \leq 0.01$) following Spring 2000, whilst soil type remained highly significant.

Microcosms treated with H_2SO_4 showed decreasing pH with increasing treatment loads (Fig. 2). Initially, the calc-silicate soil maintained the highest leachate pH across all treatment loads. At the highest levels of acid addition a trend of decreasing pH with time was evident for all soils. However, pH increased with time for control and lower acidity treatments, especially for the quartzite soil, which may arise from an initial adjustment to higher experimental base cation inputs compared with natural field inputs. The drop in drainage water pH (on 18.07.00) follows a dry period, resulting in lower dilution of treatments by precipitation. At this sampling drainage waters for all soil types under the highest acid treatments (A5) approached pH 2.5. This trough in pH was not observed for ammonium treated microcosms. In contrast to acid treatments the $(NH_4)_2SO_4$ treatments resulted in overall pH increases for quartzite and granite soil leachates. However, the pH response of the calc-silicate soil was markedly different and more similar to that observed under acid treatments. There was no evidence of seasonal patterns in pH for either acid or ammonium treated leachates.

Base cation leaching was initially accelerated by acid and ammonium treatments, followed at the highest loads by a decrease in leachate concentrations of Ca and Mg as internal production mechanisms were depleted. No clear seasonal patterns of biological uptake were apparent for these nutrient cations. Seasonality in drainage water Na^+ concentrations

Table 3. The initial (a) chemical and (b) mineralogical/physical characteristics of the soils.

(a)			*Exchangeable cations in $mmol_c\ kg^{-1}$ (means ± 1s, n = 3)*					*% base*	*% organic*	*C:N*
Soil	*pH water*	*pH $CaCl_2$*	*Na*	*K*	*Ca*	*Mg*	*CEC*	*saturation*	*matter*	*ratio*
Calc-silicate	5.32	4.24	0.2 ± 0.0	1.1 ± 0.1	4.9 ± 1.2	1.8 ± 0.1	89 ± 3.6	9.1	6.4	15
Quartzite	4.10	3.17	0.6 ± 0.0	2.0 ± 0.3	6.5 ± 0.7	4.8 ± 0.3	154 ± 11	9.1	21	26
Granite	4.09	3.20	0.5 ± 0.1	0.8 ± 0.0	0.9 ± 0.1	1.5 ± 0.2	145 ± 9.1	2.5	19	30

(b)	*% mineral compositions*							*% size fractions(μm)*		
Soil	*Quartz*	*K-feldspar*	*Albite*	*Hornblende*	*Biotite*	*Dioctahedral clays*	*Trioctahedral clays*	*60-2000*	*2-60*	*<2*
Calc-silicate	50	6.2	12	4.4	11	7.9	10	51	35	6
Quartzite	47	9.5	9.8	0	0	9.4	0	42	24	12
Granite	52	20	7.7	0	0	2.4	0	29	33	21

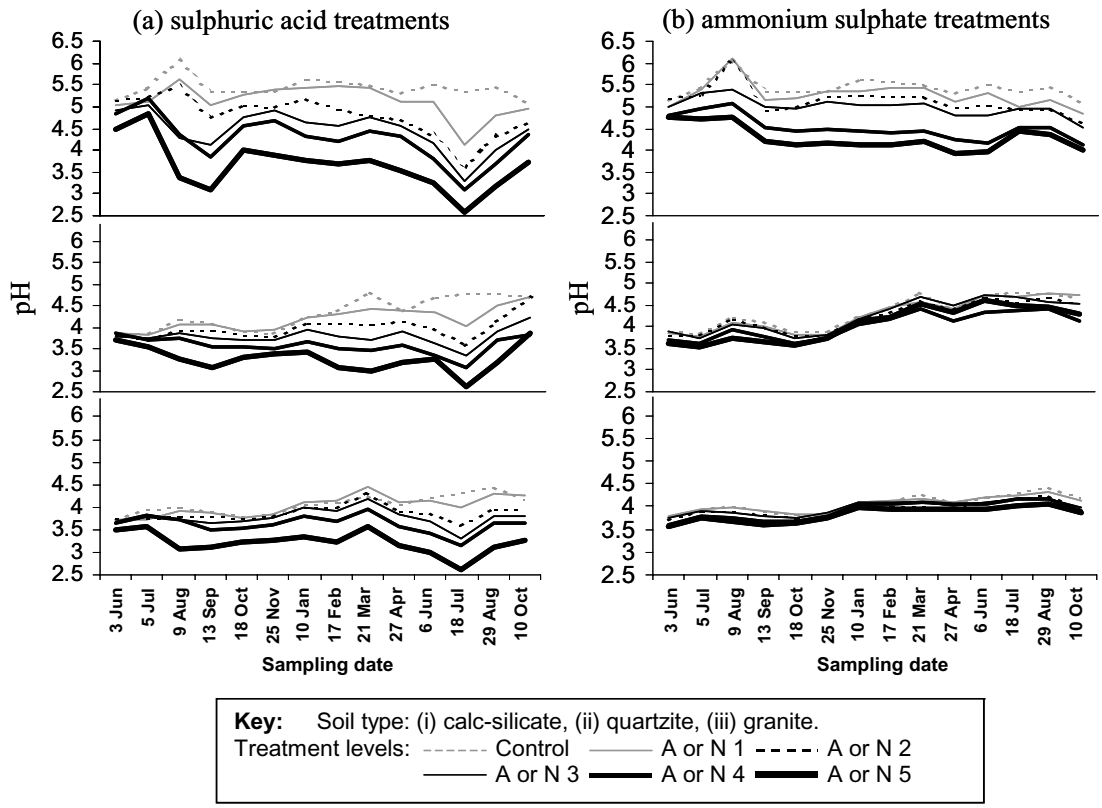

Fig. 2. *Temporal variability in drainage water pH of (a) sulphuric acid and (b) ammonium sulphate treated soils. The key depicting soil types and treatment loads given in this figure is common to figures 2-6.*

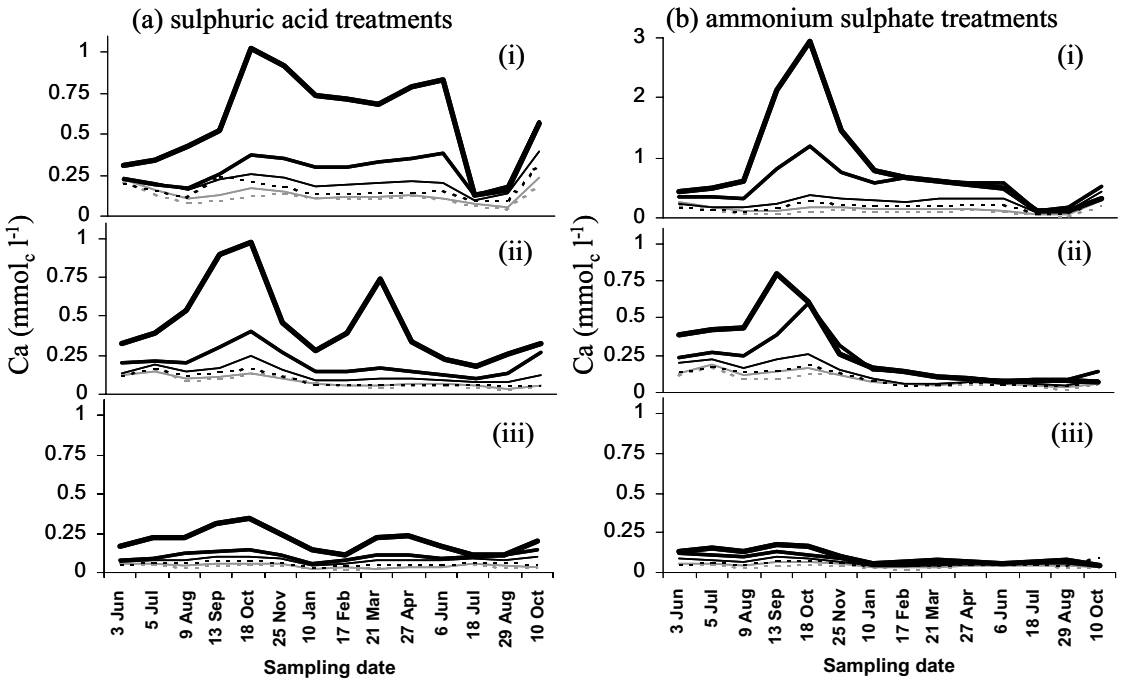

Fig. 3. *Temporal variability in drainage water Ca of (a) sulphuric acid and (b) ammonium sulphate treated soils.*

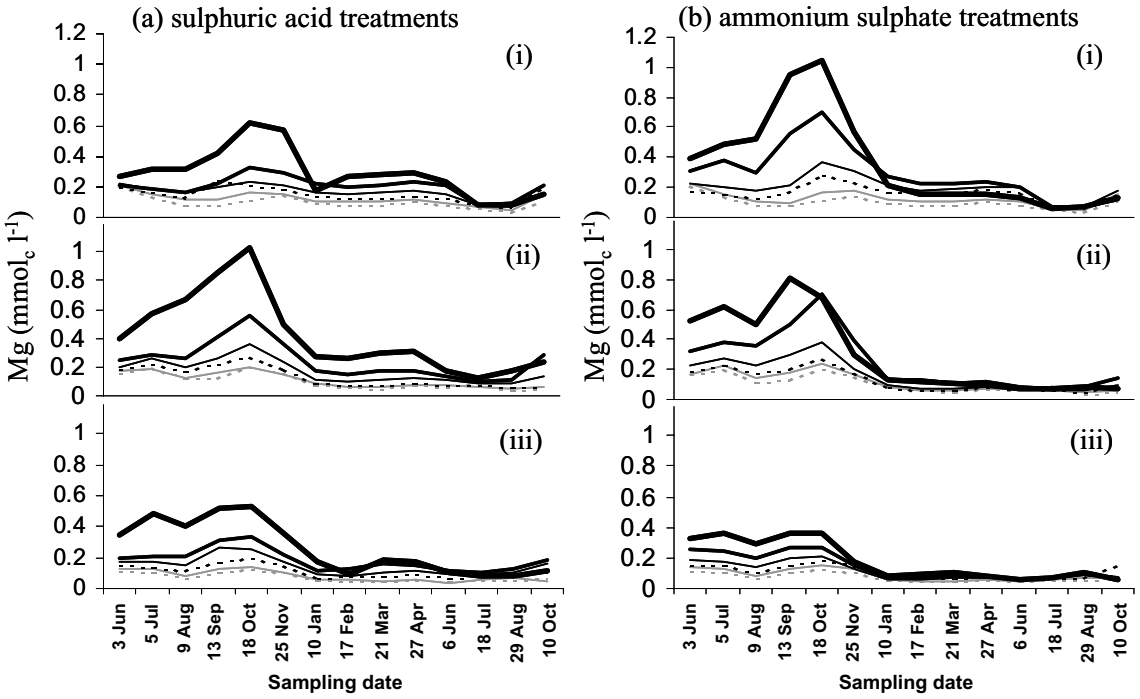

Fig. 4. Temporal variability in drainage water Mg of (a) sulphuric acid and (b) ammonium sulphate treated soils.

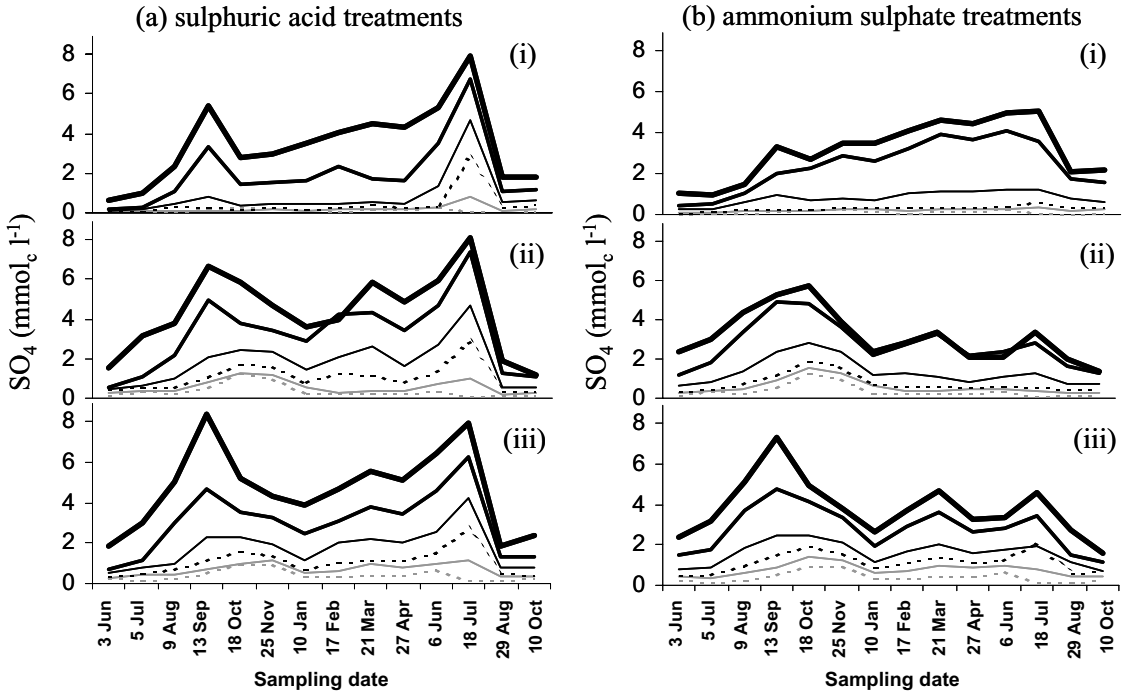

Fig. 5. *Temporal variability in drainage water SO_4 of (a) sulphuric acid and (b) ammonium sulphate treated soils.*

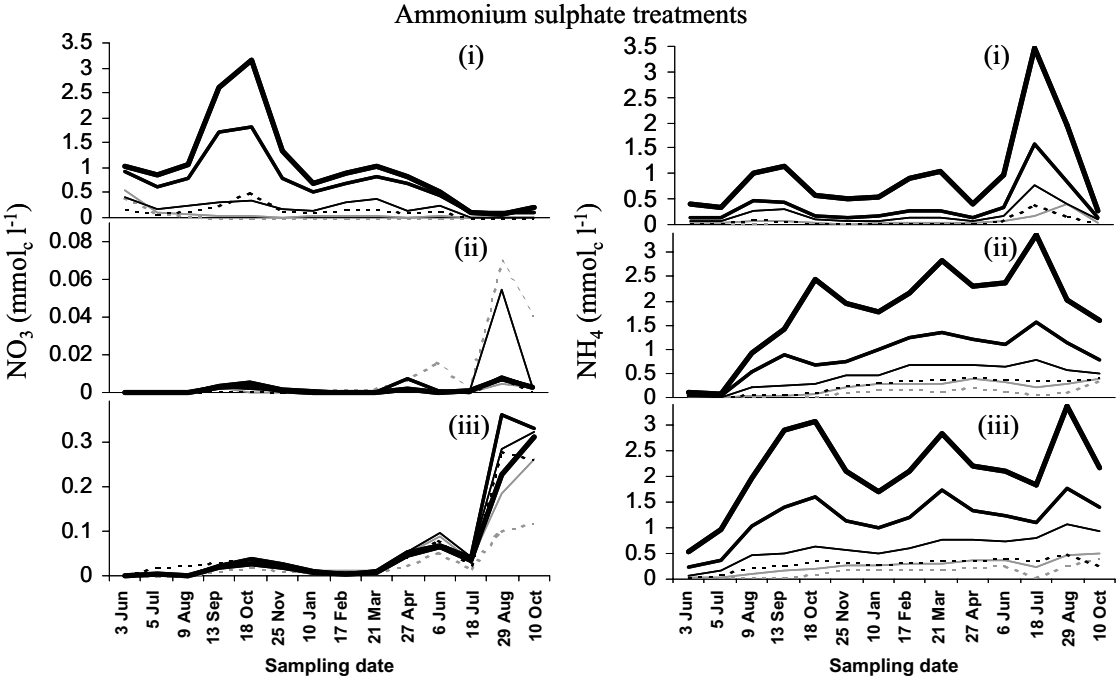

Fig. 6. *Temporal variability in drainage water (a) NO_3 and (b) NH_4 of ammonium sulphate treated soils only (note different scales used between soil types).*

mirrored those of ambient deposition, indicating atmospheric rather than internal sources. Calcium leaching (Fig. 3) demonstrated clear differences between treatments and soil types. For instance, for calc-silicate soils Ca leaching was greater under ammonium sulphate treatments than acid treatments, with significantly greater Ca leaching over controls at ³N2 levels. Conversely, Ca leaching for quartzite and granite soils was greater for acid treatments, although significantly higher concentrations than controls were only sustained by A5 treatments. Leachate Ca concentrations for N5-treated calc-silicate and quartzite microcosms dropped below those of N4 loads following autumn 1999, suggesting depletion of internal Ca sources through leaching at N5 loads, or significant biological uptake. Dry periods (09.08.99 and 21.03.00, Fig. 1) triggered elevated Ca concentrations for sulphuric acid treatments as lower treatment dilution likely enhanced Ca mobilisation. The temporal response of Mg leaching (Fig. 4) was similar to that of Ca, although the second concentration peak observed for Ca was absent in the case of Mg leaching. Similarly to Ca, ammonium treatments triggered greater leaching of Mg from calc-silicate soils (≥N2 loads), than acid treatments (>A4 loads). However, in terms of Mg leaching in granite and quartzite microcosms, similar responses were observed between treatment types (significantly elevated Mg at ≥A4/N4 loads compared to controls). Also, in contrast to Ca elevated Mg leaching at these higher treatment levels was sustained throughout the experiment.

Elevated leaching of K and Na initially observed at the higher levels of both treatment types was short-term, indicating the rapid leaching of these species from all the soils. Significantly higher leaching of K compared with controls ($p \leq 0.05$) occurred for the calc-silicate and quartzite soils at >N4 and >A4 loads for six months and for three months at N5 and A5 loads for the granite soil. Elevated leachate concentrations of Na compared to controls were only significant over the first six months for all soils at treatment loads ≥A3 and ≥N3.

As sulphate is the major anion in both treatments, the leachate concentrations (Fig. 5) reflected treatment loads and SO_4 was the dominant mobile anion in all microcosms. Whilst sulphate inputs in A5 were higher than N5 treatments (Table 2) there was less difference initially between output concentrations. Lower sulphate leachate concentrations were observed for the calc-silicate soil. Seasonality in leachate sulphate concentrations was strongly influenced by the effects of periods of low precipitation and evaporative concentration on applied treatments. The calc-silicate soil, in response to ammonium treatments N4 and N5, demonstrated a steady increase in sulphate concentrations, culminating on the 18.07.00, followed by a sharp decline. Peaks in the sulphate output of the acid treated soils

correlated to pH response (Fig. 2), with pH troughs associated with elevated SO_4 concentrations on the 13.09.99 and 18.07.00, for higher treatments. Although an early peak in Ca and Mg leaching (Figs. 3 and 4) corresponded with elevated concentrations of this key mobile anion, later peaks in SO_4 did not trigger the same response.

Leachate NO_3 concentrations of all H_2SO_4 treated soils (not shown here) remained low, with no significant effects of soil type, or treatment level. Conversely, NO_3 concentration differences between soil types (Fig. 6a) suggest differences in the ability of the soils to nitrify the treatment N inputs. The calc-silicate leachate exhibited the highest NO_3 concentrations, correlating positively with increasing ammonium treatment loads and inversely with NH_4 leachate concentrations (Fig. 6b) and coinciding with increased base cation leaching and the onset of lower pH. Leachate concentrations of NH_4 for the ammonium treated calc-silicate microcosms remained lower than for the other soils, until the onset of a large concentration peak in late summer of the second year during a dry period. A flush of NH_4 was observed from quartzite and granite microcosms at the highest acid treatments on the first rainstorm after summer in both years, suggesting mineralisation of soil organic matter in the warmer, drier period. Phosphate concentrations in drainage waters remained consistently below the detection limit of 0.1 mg (P) l^{-1}, with the exception of the calc-silicate soil during autumn of the first year (maximum values of 0.31 and 0.58 for N5 and N3 treatments respectively).

Drainage water concentrations of total Al showed considerable seasonal variability. Within this variability, the quartzite soil showed a small general concentration decline and the calc-silicate soil a larger increase with time. Concentrations were similar across lower treatment loads, but were elevated for granite microcosms at A5 loads and for the calc-silicate soil under A5 and ≥N4 loads. Peaks in Al concentrations for calc-silicate soil (spring 2000) did not correspond with peaks seen in Ca, Mg or mobile anion concentrations. Generally, total Al concentrations in leachates did not follow treatment inputs at lower loads.

MICROCOSM LEACHING FLUXES

Figure 7 depicts leachate ion fluxes and pH plotted against treatment loads. Fluxes represent total outputs for the experimental period scaled to annual values for comparison with treatment loads. Sulphate fluxes (Fig. 7a) show that all soil × treatment combinations exhibited rapid leaching increases with inputs up to 10–15 $kmol_c\ ha^{-1}\ yr^{-1}$ (A4 and N4 loads). For the quartzite and granite microcosms, this indicated a net release of SO_4 (above the indicated 1:1 line), whilst the highest acid load (A5) indicated net retention. Calc-silicate microcosms showed the lowest SO_4 fluxes, with a clear difference between H_2SO_4 and $(NH_4)_2SO_4$ treatments, suggesting acid treated soils showed an ability to retain SO_4 which was not apparent with ammonium as the accompanying cation.

Mean output fluxes of NH_4 (Fig. 7b, with the 1:1 line showing equivalent leaching of NH_4 inputs for N-treated soils) for $(NH_4)_2SO_4$ treated quartzite and granite microcosms plotted close to the 1:1 line, whereas considerable consumption of applied NH_4, was observed for calc-silicate microcosms. All acid treated microcosms showed low overall fluxes of NH_4 compared to N-treated equivalents. The quartzite and granite microcosms showed a consistent flux of NH_4 across all acid treatment loads, suggesting mineralisation of soil organic matter. Nitrate fluxes for $(NH_4)_2SO_4$ treated calc-silicate microcosms increased linearly (positive correlation; $p \leq 0.001$) up to 8 $kmol_c\ ha^{-1}\ yr^{-1}$ (N5 loads), but remained less than 0.5 $kmol_c\ ha^{-1}\ yr^{-1}$ for all other soil treatment combinations.

The highest mean leachate pH responses to treatment loads were observed for calc-silicate microcosms (Fig. 7c) where mean pH decreases were near-linearly related to $(NH_4)_2SO_4$ loads, but exponentially related to H_2SO_4 loads indicating rapid pH decreases with lower additions of acid. For the granite and quartzite microcosms pH decreases were less under higher $(NH_4)_2SO_4$ loads (>N3) compared with equivalent acid loads, although at lower loads they were more comparable between treatment types. Highly significant ($p \leq 0.001$) positive correlation was observed between mean pH and mean SO_4^{2-} leaching flux for all soil treatment combinations except for the acid treated calc-silicate microcosms ($p > 0.05$).

Treatment loads and fluxes of Ca (Fig. 7d) and Mg were positively related ($p \leq 0.05$) for all soil treatment combinations. Leaching fluxes of Ca for calc-silicate microcosms were much greater in response to combined SO_4 and NH_4 in N treatments than equivalent S loads as H_2SO_4. For other soil types, similar mean Ca fluxes were observed under either treatment type. Both Ca and Mg mean fluxes displayed highly significant ($p \leq 0.001$) negative correlation with pH and positive correlation with mean SO_4 flux for all soil treatment combinations. Mean Al fluxes (Fig. 7e) for the acid treated microcosms were increased dramatically for calc-silicate and granite soils at ≥A3 and ≥A4 loads respectively. Limited response of the quartzite soil was observed at any treatment type, or load. For $(NH_4)_2SO_4$ treatments mean Al fluxes for calc-silicate microcosms were greatly elevated by loads ≥N3, but minimal effects were observed for other soil types. Leaching of K showed minor differences between treatment type, with

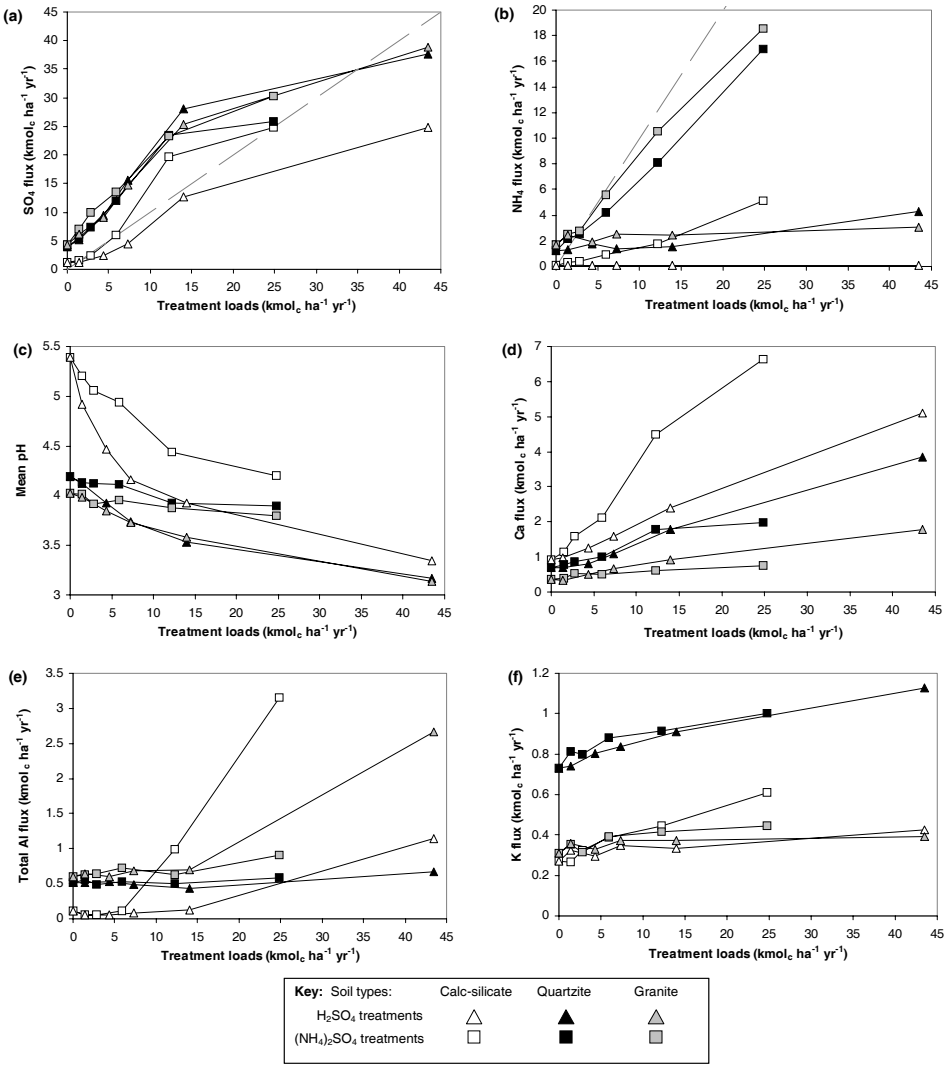

Fig. 7. *Drainage water cation and anion fluxes and mean pH over the duration of the 18 month treatment experiment plotted against treatment loads for both sulphuric acid and ammonium sulphate treatments.*

slightly elevated mean fluxes in response to $(NH_4)_2SO_4$ compared with equivalent H_2SO_4 treatments for calc-silicate and granite microcosms. Higher mean fluxes of K were observed from the quartzite microcosms, which were comparable between treatment types.

SEEDLING RESPONSE

Seedling height and stem base diameter increments were significantly affected by soil type, being greatest in calc-silicate soils and least in granite soils (Tables 4 and 5). Neither treatment type, nor treatment load had any affect on these growth parameters (Table 5). Soil type also significantly affected foliar chlorophyll a content, which was greatest in seedlings in calc-silicate soil (Table 5). Treatment load was a significant factor within both treatment types, although no individual treatment loads gave chlorophyll results significantly different from controls (Tukey simultaneous tests, $p > 0.05$). The trend was for increasing chlorophyll a with increasing acid treatment load in granite and quartzite microcosms. There was also high chlorophyll a in seedlings in these soils receiving the N load of $(NH_4)_2SO_4$. No significant differences were observed for chlorophyll b content between soil, or treatment type or load.

Elemental composition of current year needles of seedlings grown under both treatment types was strongly influenced by soil type, except for Na (Table 5). Seedlings grown in calc-silicate soil had markedly lower foliar K, lower N, much higher P and slightly higher Mg concentrations than those grown in the other two soils (Fig. 8). Granite microcosms had lower foliar Mg and Ca concentrations than quartzite microcosms.

Table 4. Effects of soil type (within each treatment type) on seedling height and stem base diameter increments (across all treatment levels, including controls) after the first (1999) and second (2000) growth seasons. Different superscript letters denote differences between soil type means within growth measurement classes ($p \leq 0.05$).

	Height increment (cm)		*Diameter increment (cm)*	
Soil type	*1999*	*2000*	*1999*	*2000*
SULPHURIC ACID TREATMENTS				
Calc-silicate	10.4^{a}	35.6^{a}	0.26^{a}	0.87^{a}
Quartzite	9.04^{ab}	19.4^{b}	0.18^{b}	0.32^{b}
Granite	8.68^{b}	16.6^{b}	0.13^{c}	0.26^{b}
AMMONIUM SULPHATE TREATMENTS				
Calc-silicate	11.1^{a}	34.3^{a}	0.30^{a}	0.86^{a}
Quartzite	10.3^{a}	19.2^{b}	0.19^{b}	0.32^{b}
Granite	8.42^{b}	17.1^{b}	0.18^{b}	0.32^{b}

The only significant effects of acid treatment were overall trends for decreasing foliar K and Mg with increasing acid load, particularly >A3 (Fig. 8a, Table 5). Ammonium sulphate treatments affected more elements, with overall trends of decreasing foliar Mg, Ca, K and P with increasing treatment load (Fig. 8b, Table 5). Significant interactions with soil type reflect that the decrease in foliar Mg was strongest, and the decrease in P only occurred, in calc-silicate microcosms (in which Mg in N4 and N5, and P in N5, differed significantly from the control). Foliar N concentration was not affected by $(NH_4)_2SO_4$ treatment load, and was only marginally greater in the $(NH_4)_2SO_4$ treated than in the acid treated seedlings (in granite and quartzite soil).

Discussion

SOIL ACIDIFICATION MECHANISMS AND EFFECTS

The experiment was long enough to exhaust initial buffering by cation exchange and see the different capacities of the soils to buffer through mineral weathering. It also showed the strong effects of ambient precipitation on leachate compositions. Soil acidification was manifested in decreased leachate pH and enhanced leaching of base cations. The extent to which a soil is affected depends on its ability to buffer against accelerating base cation leaching and increasing dominance of acid cations. The leaching accelerates due to direct exchange with treatment cations (H^+, or NH_4^+), from higher solution concentrations of the mobile treatment anion SO_4^{2-}, or acidity generated through biological N transformations and nutrient uptake. The timescales of exhausting short-term acid buffering capacities of the soils clearly differed between soil type and in response to treatment type. The higher loads of H_2SO_4 for all soils resulted in increasingly lowered pH with continuing treatment. However, $(NH_4)_2SO_4$ treatments only lowered leachate pH in calc-silicate microcosms, whilst resulting in increased pH in quartzite and granite soils. Soil leachate compositions initially reflected the constituent cations on the soil ion exchange sites. The subsequent replenishment of exchangeable base cations then depended on mineral

Table 5. Results of two-way ANOVA exploring effects of soil type, treatment level and soil treatment interactions on seedling growth (measured 1999 and 2000) and chemical parameters (determined in 2000 only) as a result of (i) sulphuric acid and (ii) ammonium sulphate treatments.

	Dependent variables											
Factors	*Height*		*Diameter*		*Chl. a*	*Chl. b*	*Na*	*K*	*Ca*	*Mg*	*N*	*P*
	1999	*2000*	*1999*	*2000*								
(i) SULPHURIC ACID TREATMENTS												
Soil type	**	***	***	***	***	ns	ns	***	***	***	***	***
Treatment	ns	ns	**	ns	*	ns	ns	*	ns	*	ns	ns
Soil * treatment	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
(ii) AMMONIUM SULPHATE TREATMENTS												
Soil type	***	***	***	***	***	ns	*	***	***	***	***	***
Treatment	ns	ns	ns	ns	*	ns	ns	*	***	***	ns	**
Soil * treatment	ns	ns	ns	ns	ns	ns	ns	ns	ns	**	ns	*

Significance levels: *** $p \leq 0.001$, ** $p \leq 0.01$, * $p \leq 0.05$, ns = not significant

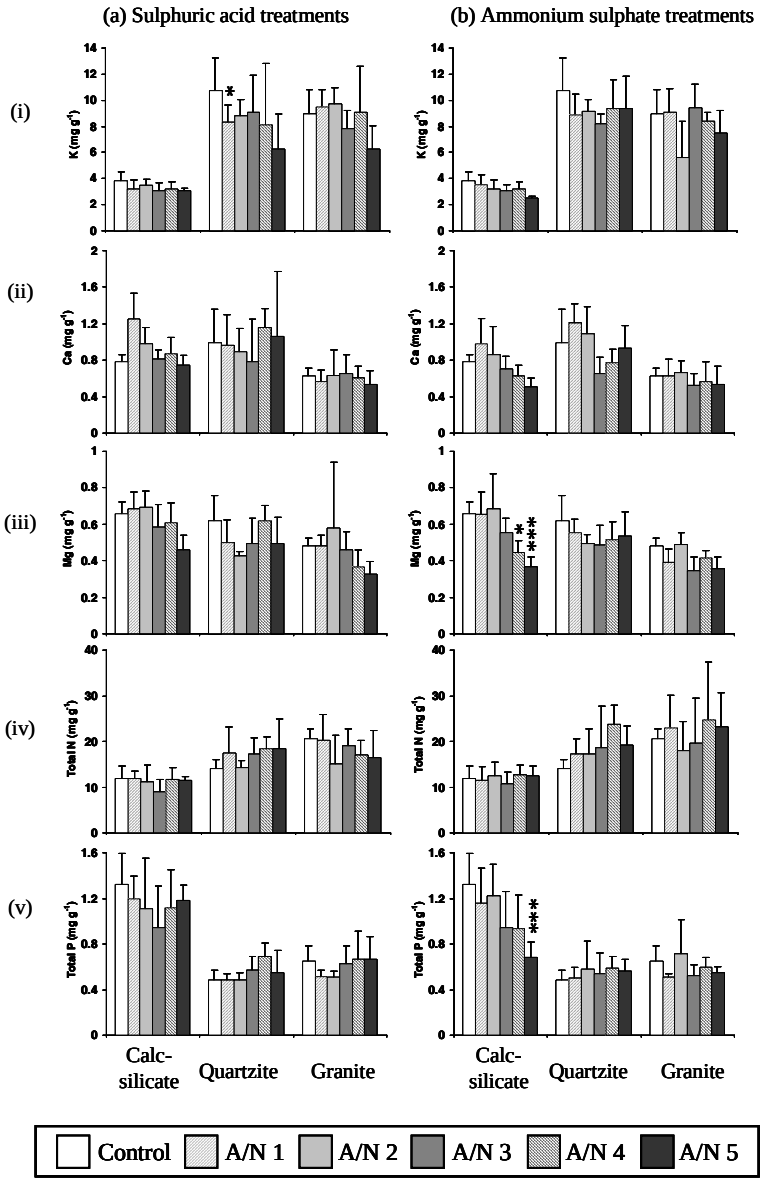

Fig. 8. *The effects of (a) sulphuric acid and (b) ammonium sulphate treatment levels on seedling mean foliar content (±1s error bars) of (i) K, (ii) Ca, (iii) Mg, (iv) total N and (v) total P (mg g^{-1} of dry mass material). Significant differences between seedlings in treated microcosms compared to control microcosms are given as * $p \leq 0.05$, *** $p \leq 0.001$ and no symbol denotes not significant.*

weathering. The soil mineralogy (Table 3b) suggests that reactive minerals (hornblende and biotite) present in the calc-silicate soil will have a greater potential to buffer through weathering and sustain leachate base cation concentrations.

White and Cresser (1998a) observed steady increases in leachate concentrations of all base cations in response to 20 weeks simulated wet deposition inputs of $(NH_4)_2SO_4$ onto a granitic soil at loads up to the equivalent of N4 levels used here. In the present study, $(NH_4)_2SO_4$ treated soils showed initial peaks in Ca and Mg leaching during the first year (Figs. 3 and 4), related to initial exchange site base cation saturation (Table 3a). In the granite and quartzite microcosms, minimal leaching of these base cations after the first year resulted from less reactive soil minerals. For the calc-silicate microcosms, soil minerals were able to supply Ca and Mg at smaller, but sustained concentrations, the proton sources for mineral hydrolysis in this case being related in part to biological transformations of the reduced N inputs. However, buffering was insufficient to ameliorate the continued decline in leachate pH for calc-silicate microcosms. The leachate pH increases for granite and quartzite microcosms, even for controls, were likely due to a re-equilibration with the enhanced base cation deposition, especially for Ca, between the natural deposition at the

upland collection site and that of the combined experimental site ambient and treatment inputs (Table 2).

The H_2SO_4 treated soils, by contrast, tended to maintain higher Ca and Mg leaching (Figs. 3 and 4) longer into the second year. After the initial peak outputs related to H^+ and SO_4^{2-} concentrations in solution the continued proton inputs were able to hydrolyse minerals and maintain Ca and Mg supply from primary minerals in the calc-silicate soil and Mg from secondary minerals in the quartzite and granite soils (Table 3b). Rapid declines in leachate K were observed for all soils (despite the high composition of K-feldspar in the granite soil) although this probably also reflects biological uptake. Despite the different mineral and organic compositions of the soils the leachate pH decreases over time in response to acid treatments were similar.

Fluctuating concentrations of Na^+ suggested the dominant role of atmospheric over internal inputs for this cation as described above. Decreases in divalent cation leaching with time, increasing the relative dominance of Na amongst base cations, were common to both H_2SO_4 and $(NH_4)_2SO_4$ treated soils supporting previous observations made for mineral soils (White and Cresser, 1998a) and peats (Yesmin, 1995). This enhanced buffering by marine-derived cations shows the importance of including them in such experimental systems.

The mineral or organic nature of the exchange sites may control the concentrations and competitive release dynamics of adsorbed cations. For quartzite microcosms, higher levels of organic matter were likely responsible for greater reserves of divalent basic cations than anticipated by the mineralogy (Table 3). More abundant organic material in the quartzite and granite microcosms also provided considerable sources of exchangeable acid proton and Al species, with additional weathering sources of Al from minerals. Longer-term contributions of acid cations on exchange sites as indicators of soil acidification may be reflected in decreased pH. However, for the calc-silicate microcosms, enhanced Al leaching with $(NH_4)_2SO_4$ treatment, compared with equivalent SO_4 loads as H_2SO4, was apparent. Consideration of solution pH in isolation would thus underestimate ammonium treatments effects on elevated Al leaching, which occurred at higher solution pH than in response to acid treatments.

Reduced dilution of applied treatments during periods of low ambient precipitation (Fig. 1) triggered peaks in SO_4 concentration for both treatment types and gave rise to the lowest troughs in leachate pH for acid treated soils in Summer. For all soil and treatment combinations, these periods resulted in considerable mobilisation of Ca and Mg, with subsequent flushing from the microcosms by the next precipitation event. The ability of mobile anions such as SO_4 to enhance base cation leaching is well documented (e.g. White and Cresser, 1998b). Hence, a soil's ability to adsorb sulphate provides a mechanism that potentially buffers against soil acidification in response to atmospheric pollution (Eriksson, 1988; Gustafsson and Jacks, 1993). Nodvin *et al*. (1986) showed that soil SO_4 adsorption capacity increased with decreasing pH and results here for the higher acid treatments support this. However, Inskeep (1989) reported that organic matter inhibited adsorption capacity due to competitive adsorption of organic anions. In the present study this may have limited sulphate retention buffering in quartzite and granite microcosms.

Mean sulphate fluxes (Fig. 7a) indicated net retention of sulphate for acid treated calc-silicate microcosms, with net outputs indicated for all other soil and treatment combinations. These net gains may be related to the mineralisation of soil organic matter in quartzite and granite soils. A capacity for longer-term SO_4 adsorption in the calc-silicate soil is indicated at loads <A3/N3 (Fig. 5), where SO_4 leachate concentrations remain much lower than for quartzite and granite soils. At higher treatments (≥A3/N3) calc-silicate SO_4 leachate concentrations steadily increase indicating decreasing buffering. However, SO_4 adsorption appeared insufficient to mediate pH declines in calc-silicate microcosms, even though Wilson and Skeffington (1994) found this mechanism strongly buffered acidity in soils treated with ammonium sulphate at loads similar to those in this experiment. The levels of NO_3 leaching in this soil also contribute to the mobile anion effect.

Ammonium was the dominant cation output from the quartzite and granite microcosms (Fig. 6b), whilst divalent basic cations dominated outputs from N-treated calc-silicate microcosms with minimal NH_4 output. Given the elevated leaching of NO_3 from the calc-silicate microcosms (Fig. 6a), nitrification most likely explains NH_4 losses, with the 2 moles of protons produced during nitrification of 1 mole of NH_4 (Van Breemen *et al*., 1982) contributing to the enhanced rate of base cation leaching and low pH. Van Breemen *et al*. (1982) highlighted the rapid nitrification of reduced N from ammonium sulphate deposition in relatively nutrient-rich soils. Conversely, Gundersen and Rasmussen (1988) showed that in nutrient-deficient soils with low biological turnover, excess ammonium deposition was leached. Ste-Marie and Paré (1999) observed that vegetation, soil type, temperature, pH and substrate and nutrient availability controlled nitrification. Their study established relationships between solution pH and nitrification rates in a range of forest soil and concluded that nitrification was limited below pH 4.5. In the present study, calc-silicate microcosms generally maintain pH >4.5, whilst quartzite and granite microcosms are suggested as unfavourable for nitrification. Another

factor likely to affect nitrification is the original nitrifying microbial communities under different vegetation types. The calc-silicate soil was collected from grassland, but the granite and quartzite soils were from *Calluna*-dominated moorland, which may support nitrification rates an order of magnitude lower than for grassland ecosystems (Van Vuuren *et al*., 1992).

BIOLOGICAL RESPONSE

An important measure of sustained soil functioning in response to acidification is the ability to supply nutrients required for plant growth. Several factors may have contributed to the impaired growth observed for seedlings in quartzite and granite microcosms compared with those in calc-silicate microcosms. Firstly, the availability of Ca and Mg became limited in quartzite and granite microcosms after heavy rain at the end of the first year. This was especially pronounced for Ca availability in granite microcosms, contributing to the slowest growth and giving the lowest seedling foliar Ca concentrations in both treatment types at all levels. Secondly, significantly lower foliar P concentrations were observed in seedlings grown in quartzite and granite soils, which are suggested to be P deficient in both treatment types compared to the critical concentration of 2 mg (P) g^{-1} proposed by Miller (1986). That low P was observed for control and treated quartzite and granite microcosms suggests that this was not a treatment effect, but may rather have limited the effects of treatments on seedling on these soil types. Another soil-plant nutrient link was greater foliar concentrations of chlorophyll a in calc-silicate microcosms, likely related to higher Mg availability.

The availability of increased NO_3 in N-treated calc-silicate microcosms may have stimulated greater cation uptake (previously observed by Marschner, 1995), although overall seedling growth was no different for this soil in either treatment type. Lower foliar K and N concentrations in calc-silicate microcosms may be explained by dilution in tissues from rapid growth. Ammonium treatments did not have any effect on foliar N concentrations, despite previous observations of enhanced pine and spruce growth and reduced foliar cation concentrations as a result of excess N deposition in forest ecosystems (Song and Abrahamsen, 1998; Houdijk and Reolofs, 1993; Van Dijk *et al*., 1990). The present results suggest that N availability may be less important than other soil related factors, such as P limitation, which may limit the positive effects of enhanced N deposition. Phosphorus deficiency may have been compounded by an absence of the natural soil litter layer since this was excluded on soil collection and comprises a potentially important source of readily available organic N and P nutrients. The only major effect of treatment load on foliar composition was related to Mg and P reductions for N5 treatments of calc-silicate soils, which since not related to dilution into greater biomass at higher treatment loads, may be related to nutrient leaching losses from the soil.

QUANTIFYING TREATMENT CRITICAL LOADS FROM SOIL AND SEEDLING EFFECTS

Acid treatment of the examined soils initially significantly elevated Ca and Mg leaching compared to controls at loads ≥A4 (14 $kmol_c$ ha^{-1} yr^{-1}), with pH significantly lowered at loads ≥A3 (7.3 $kmol_c$ ha^{-1} yr^{-1}). Ammonium treatments triggered significant base cation leaching in calc-silicate soils at ≥N2 loads (1.45 $kmol_c$ ha^{-1} yr^{-1}), but whilst quartzite soils showed significant leaching of Ca and Mg at ≥N4 (12.2 $kmol_c$ ha^{-1} yr^{-1}) concurrent increases were observed in leachate pH with time.

Wilson and Skeffington (1994) discussed the complexities in addressing N contributions to acidification and examined certain critical chemical values relating to soil damage indicators from the literature in order to provide a basis for estimation of critical loads. Time-averaged values from the present study have been calculated for these chemical criteria in order to highlight loads at which adverse affects of the treatments may be assessed using these literature thresholds (Tables 6a and 6b). Time-averaged data across the entire experimental period are used to encompass the long-term effects of treatments across different seasons and where values exceed the literature threshold values these are given in bold text.

Nilsson and Grennfelt (1988) used molar ratios of NH_4 with K or Mg as indices of the competitive inhibition of nutrient uptake by NH_4. The ratios of 5 and 10 respectively for N/K and N/Mg as critical for forest soil health. Data from the N-treated microcosms in the present study (Table 6b) showed that this threshold N/K value was exceeded in calc-silicate and quartzite microcosms ≥N3 loads (5.93 $kmol_c$ ha^{-1} yr^{-1}, or 83.1 kg (N) ha^{-1} yr^{-1}). Granite microcosms exceeded this critical value in all acid and ammonium loads including controls, demonstrating the high mobility and rapid depletion of exchangeable K reserves. Critical N/Mg values were exceeded for calc-silicate microcosms at N5 loads (24.8 $kmol_c$ ha^{-1} yr^{-1}, or 347 kg (N) ha^{-1} yr^{-1}) and at ≥N3 loads (5.93 $kmol_c$ ha^{-1} yr^{-1}, or 83.1 kg (N) ha^{-1} yr^{-1}) for the other soils, as a result of greater ammonium leaching. In a study by Wilson and Skeffington (1994), in which acid brown soils were treated with ammonium sulphate, these thresholds were exceeded at higher loads of ≥60 and ≥120 kg (N) ha^{-1} yr^{-1}, for N/K and N/Mg respectively. Wilson and Skeffington (1994) give critical values for NO_3 and total N

Table 6. Mean data for pH and key factors indicated as being critical to assessing soil 'damage' in pollution studies. Data presented from (a) the acid treatments and (b) the ammonium treatments. Bold type indicates values that exceed critical levels taken from other studies in the literature.

(a)	*Treatment loads*	*A0*	*A1*	*A2*	*A3*	*A4*	*A5*
	kmol$_c$ ha^{-1} yr^{-1}	0	1.4	4.4	7.3	14	44
	kg H ha^{-1} yr^{-1}	0	1.4	4.4	7.3	14	44
Calc-silicate							
	pH	5.39	4.92	4.47	4.16	3.93	3.34
	Ca:Al$_{total}$	20.8	17.3	20.8	16.3	20.3	7.37
	NH_4(N) / K ratio	0.27	0.29	0.29	0.32	0.26	0.35
	NH_4(N) / Mg	0.07	0.21	0.21	0.11	0.12	0.17
	Max NO_3 (mg l^{-1})	**26.5**	**27.7**	**27.5**	**21.7**	**21.6**	**14.8**
	Max N leach (mg l^{-1})	**6.18**	**6.46**	**6.63**	5.08	5.09	3.63
Quartzite							
	pH	4.19	4.12	3.93	3.74	3.53	3.17
	Ca:Al$_{total}$	1.11	1.11	1.14	1.63	2.65	3.52
	NH_4(N) / K ratio	2.29	2.63	3.13	2.27	2.55	**6.20**
	NH_4(N) / Mg	2.30	2.84	4.46	3.03	2.29	4.02
	Max NO_3 (mg l^{-1})	**4.27**	0.08	0.16	**1.47**	0.28	0.17
	Max N leach (mg l^{-1})	**5.60**	4.88	**5.76**	3.81	4.23	**10.1**
Granite							
	pH	4.02	3.98	3.85	3.73	3.58	3.14
	Ca:Al$_{total}$	**0.36**	**0.33**	**0.48**	**0.53**	**0.79**	**0.46**
	NH_4(N) / K ratio	**5.71**	**5.39**	**6.93**	**10.1**	**8.65**	**9.38**
	NH_4(N) / Mg	3.47	7.91	6.52	4.83	3.91	3.40
	Max NO_3 (mg l^{-1})	**7.30**	**11.6**	**16.7**	**19.1**	**6.67**	**3.20**
	Max N leach (mg l^{-1})	**7.21**	**9.45**	**10.1**	**12.5**	**6.80**	**11.1**

(b)	*Treatment loads*	*N0*	*N1*	*N2*	*N3*	*N4*	*N5*
	kmol$_c$ ha^{-1} yr^{-1}	0	1.5	2.8	5.9	12	25
	kg N ha^{-1} yr^{-1}	0	20	39	83	171	347
Calc-silicate							
	pH	5.39	5.20	5.06	4.94	4.44	4.20
	Ca:Al$_{total}$	20.8	19.5	24.1	22.6	16.4	10.0
	NH_4(N) / K ratio	0.27	4.43	4.35	**9.10**	**15.9**	**37.0**
	NH_4(N) / Mg	0.07	1.27	2.04	3.90	6.98	15.4
	Max NO_3 (mg l^{-1})	**26.5**	**34.0**	**31.7**	**24.9**	**112**	**196**
	Max N leach (mg l^{-1})	**6.18**	**8.07**	**7.47**	**10.8**	**30.1**	**52.6**
Quartzite							
	pH	4.19	4.13	4.12	4.11	3.93	3.90
	Ca:Al$_{total}$	1.11	1.13	1.65	1.77	2.54	2.65
	NH_4(N) / K ratio	2.29	3.56	4.97	**10.2**	**19.9**	**39.9**
	NH_4(N) / Mg	2.30	1.67	7.57	**11.5**	**20.2**	**28.4**
	Max NO_3 (mg l^{-1})	**4.27**	0.27	0.47	**3.39**	0.51	0.43
	Max N leach (mg l^{-1})	**5.60**	**5.37**	**5.95**	**10.9**	**22.0**	**47.3**
Granite							
	pH	4.02	4.01	3.92	3.95	3.88	3.80
	Ca:Al$_{total}$	0.36	0.42	0.52	0.47	0.66	0.57
	NH_4(N) / K ratio	**5.71**	**14.7**	**11.9**	**28.1**	**37.0**	**64.6**
	NH_4(N) / Mg	3.47	3.74	8.87	**13.7**	**27.1**	**42.1**
	Max NO_3 (mg l^{-1})	**7.30**	**16.2**	**17.4**	**19.9**	**22.3**	**19.3**
	Max N leach (mg l^{-1})	**7.21**	**10.8**	**10.9**	**18.8**	**29.8**	**50.1**

(NO_3 + NH_4) leachate concentrations, of respectively 1 mg l^{-1} NO_3 and 5.6 mg total N l^{-1}. In the present study, however, these values were commonly exceeded at low N loads and even for control treatments.

The greater fluxes of total Al resulting from $(NH_4)_2SO_4$ than H_2SO_4 treatments of calc-silicate microcosms (Fig. 7e) are important to drainage water quality. Egli and Fitze (1995) related displacement of Al into the drainage waters of field soils under high natural loads of reduced N to a high degree of nitrification. At the highest concentrations of Al they also found that organic ligands were coagulated and precipitated, elevating the proportion of more toxic inorganic species. An important index for the role of Al in forest soil 'health' is the use of Ca:Al, (or sometimes base cation:Al) molar ratios, with a value of <1 being used as an indication of Al root toxicity (Sverdrup and Warfvinge, 1993). Although in this case the use of total Al concentrations encompasses the less toxic organic as well as inorganic fractions, this critical level was exceeded only by granite microcosms, although at both acid and ammonium treatments at all levels including controls. Quartzite mean Ca:Al ratios clearly increased with elevated loads of both treatments, demonstrating that ion exchange for either H ions or NH_4 liberated more Ca than Al at least in the duration of our observations. However, current critical load methods assume steady-state conditions and thus cannot represent such important changes concerning soil exchange processes.

Conclusions

The rationale behind this study was to examine the responses of three upland soils to different treatment levels of two common components of acidifying deposition and make links to growth indicators for seedlings of a common pine species. Sulphuric acid treatments commonly promoted acidification of all soils, significantly elevating cation leaching and lowering solution pH at H_2SO_4 loads of ≥14 and ≥7.3 $kmol_c$ ha^{-1} yr^{-1} respectively. However, the effects of ammonium sulphate treatments depended on soil type. The calc-silicate soil demonstrated a markedly different leaching response, with sustained cation leaching at N loads of ≥1.45 $kmol_c$ ha^{-1} yr^{-1}, through its ability to nitrify reduced N inputs. The protons generated were responsible for more sustained acidification effects, which included elevated Al concentrations. By contrast, the initial observed short-term cation leaching for the quartzite and granite soils was attributed to an ability of the cation NH_4 and the anion SO_4 to desorb exchangeable cations only, with little proton availability for mineral hydrolysis. The lack of nitrifiers in these two soils may be related to the natural vegetation type, lower soil pH, or higher soil organic matter composition.

Differences in seedling growth between soil types were related to the presence of soil minerals able to sustain nutrient release. However, no treatment effects were observed on growth. Calc-silicate microcosms maintained higher foliar P, Mg and chlorophyll a concentrations, although N and K were lower, probably as a result of growth dilution. Granite microcosms showed the most limited growth with links to the lowest solution Ca:Al ratios, low foliar Ca compositions and competition of the treatment cation NH_4 in plant nutrient uptake. The only significant effects of treatments on foliar compositions were for ammonium treated calc-silicate microcosms for which foliar Mg and P were reduced by NH_4 deposition of 25 $kmol_c$ ha^{-1} yr^{-1} relative to controls.

The results show that critical loads for atmospheric pollution must account both for differences in a soils' abilities to sustain buffering through mineral reactions and the soil potential for transformations of deposition species. Where soil conditions allow, nitrification of reduced N deposition may be more damaging than direct effects of sulphuric acid. Minimal differences in foliar N concentrations between treatment types and levels indicate that N nutrition benefits as a result of reduced N deposition may be offset by limited availability of other nutrients, soil composition and microbial factors.

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